

LABORATORY SHOCK EXPERIMENTS ON BASALT – IRON SULFATE MIXES AT ~ 40 – 50 GPa AND THEIR RELEVANCE TO THE MARTIAN REGOLITH COMPONENT PRESENT IN SHERGOTTITES.

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Introduction: Basaltic shergottites such as Shergotty, Zagami and EET79001 contain impact melt glass pockets that are rich in Martian atmospheric gases [1] and are known as gas-rich impact-melt (GRIM) glasses. These glasses show evidence for the presence of a Martian regolith component based on Sm and Kr isotopic studies [2]. The GRIM glasses are sometimes embedded with clusters of innumerable micron-sized iron-sulfide blebs associated with minor amounts of iron sulfate particles [3, 4]. These sulfide blebs are secondary in origin and are not related to the primary igneous sulfides occurring in Martian meteorites. The material comprising these glasses arises from the highly oxidizing Martian surface and sulfur is unlikely to occur as sulfide in the Martian regolith. Instead, sulfur is shown to occur as sulfate based on APXS and Mossbauer results obtained by the Opportunity and Spirit rovers at Meridiani and Gusev [5]. We have earlier suggested that the micron-sized iron sulfide globules in GRIM glasses were likely produced by shock-reduction of iron sulfate occurring in the regolith at the time when the GRIM glasses were produced by the meteoroid impact that launched the Martian meteorites into space [6]. As a result of high energy deposition by shock (~ 40-60 GPa), the iron sulfate bearing phases are likely to melt along with other regolith components and will get reduced to immiscible sulfide fluid under reducing conditions. On quenching, this generates a dispersion of micron-scale sulfide blebs. The reducing agents in our case are likely to be H₂ and CO which were shock-implanted from the Martian atmosphere into these glasses along with the noble gases. We conducted lab simulation experiments in the Lindhurst Laboratory of Experimental Geophysics at Caltech and the Experimental Impact Laboratory at JSC to test whether iron sulfide globules can be produced by impact-driven reduction of iron sulfate by subjecting Columbia River Basalt (CRB) and ferric sulfate mixtures to shock pressures between 40 and 50 GPa under reducing conditions. The experimental products from the recovered samples were analyzed by SEM and microprobe techniques at JSC.

Experimental: About 50 mg of Columbia River Basalt (~65 μ m dia average) plus ferric sulfate (powder and chips up to 1mm dia) were mixed and heated to 110 °C in vacuum for few hrs at the Lindhurst Lab at Caltech. This mix was pressed at 2200 psi into a pel-

let of 5 mm dia and 1.17 mm thick having an estimated porosity of 28%. This CRB + ferric sulfate pellet was loaded into the cavity of stainless steel 304 sample retainer within a vented sample housing. The target assembly was placed in the target chamber of a 20 mm bore single stage gun, pumped to vacuum through the vent port and refilled with lab grade CO (used as reducing agent in this experiment). The pore space in the sample contained ~ 0.8 bars of CO gas at ambient temperature. A 2.5 mm thick SS 304 flyer was launched at a measured pre-impact velocity of 2.04 km/sec and impacted the surface of the sample holder generating a shock wave with a final reverberation pressure of 49 GPa after the estimated first two shock conditions of 14.4 GPa at 1350 K and the reshock of ~35 GPa at 2500 K. The recovered sample holder had a well defined crater with no evidence for the failure of the sample chamber or loss of sample.

The chamber was sawn open and one half of the shocked sample was impregnated with epoxy preserving in-situ spatial distribution of the reaction products and machined to fit into the FE - SEM sample holder at JSC. The top surface of the sample was then gently polished to remove epoxy and expose the shocked sample. The polished surfaces of this sample were examined under FE-SEM at JSC and the results are given below.

We carried out additional shock experiments on the same basalt plus ferric sulfate mixture at 12 GPa and 40 GPa shock pressures without purging the sample with CO to examine whether a reducing agent is required to produce iron sulfide blebs from iron sulfate during shock-melting. These samples are being processed and examined at this time.

Results: The sulfide content of CRB is low (0.05 – 0.2% S) [7]. The starting material consists of CRB dry powder mixed with an inhomogeneous distribution of powder and chunks of ferric sulfate in 2:1 overall proportion. From visual as well as SEM examination, one finds a lot of molten material in the recovered charge. In some regions of the recovered sample, however, angular and unmolten ferric sulfate crystals are found mixed with parent basalt particulates. In the case of granulated lunar basalt 75035 (45-75 microns and 40% porosity), Schaaf et al. [8] showed that shock melting of basalt material at 50 GPa transforms ~ 35 - 40% of the parental material into glass.

The FE-SEM BSE images and the corresponding EDS spectra for the sulfide blebs in a molten region and unmelted ferric sulfate particulates mixed with basalt fragments are shown in Figs. 1 & 3 (images) and Figs. 2 & 4 (spectra) respectively. In many areas of the recovered basalt charge, we noticed only a small number (~2-8 per image) of sulfide blebs along with some amount of unmelted ferric sulfate and basalt particulates. But, in a few locations, we found clusters of abundant micron-sized sulfide blebs. A typical example is shown in Fig. 1. This observation suggests that the shock wave might have propagated non-uniformly in the sample volume, with presence or absence of sulfide in an area controlled by whether the sample locally melted. However, the CO that is filling the pore volume in the sample might also have been inhomogeneously distributed during shock and this might explain the final distribution of observed sulfide. In areas where CO is available, the molten sulfate will be reduced to sulfide generating immiscible sulfide fluid that, on quenching, forms innumerable sulfide blebs. That is, reduction of sulfate may require both local high energy deposition and local availability of CO reducing agent. The significance of the local availability of CO as the controlling factor in the reduction of locally melted sulfate could be understood by searching for sulfide-free, sulfate-bearing regions with molten texture in the shocked samples from the experiments conducted at JSC without CO in the pore space.

Minitti et al. [9] carried out shock experiments at Ames gun lab on kaersutitic amphiboles at ~30-35 GPa in connection with Martian water in SNCs and showed using Mossbauer measurements that Fe^{3+} in hornblende was reduced to Fe^{2+} during shock. Also, Sutton et al. [6] studied vanadium valence states in EET79001 GRIM glasses containing micron-sized sulfide blebs and showed using micro-XANES measurements that V^{4+} in Martian basalt was reduced to V^{3+} during shock.

In conclusion, our laboratory shock experiments on basalt plus iron sulfate mixtures demonstrate the plausibility of formation of secondary micron-sized sulfide blebs from sulfate-bearing Martian regolith material in shergottite GRIM glasses by shock-induced reduction.

References: [1] Bogard D. D. and Johnson P. H. (1983) *Science*, 221, 651–654. [2] Rao M. N. et al. (2011) *JGR*, 116, E08006, doi:10.1029/2010JE003764. [3] Walton E. L. et al. (2010) *GCA*, 74, 4829 – 4843. [4] Rao M.N. et al. (2004) *LPS XXXV*, Abstract, #1501. [5] King P.L. and McLennan S. M. (2010) *Elements*, 6, 107-112. [6] Sutton S. R. et al. (2008) *LPS XXXIX*, Abstract #1961. [7] Blake S. et al. (2010) *EPSL*, 299, 328 – 338. [8] Schaal R. B. et al. (1979) *Proc. Lunar Planet. Sci. Conf.* 10th, 2547 – 2571. [9] Minitti M.E. et al. (2008) *EPSL*, 266, 46-60.

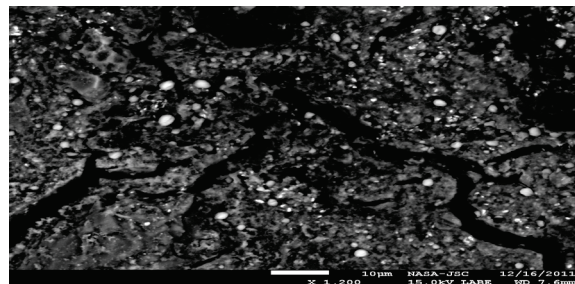


Fig. 1. BSE image of the area in the recovered sample showing abundant iron sulfide blebs along with molten iron sulfate globules.

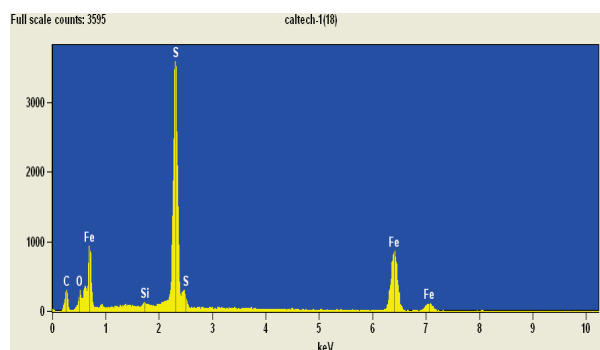


Fig. 2. Typical EDS spectrum of the iron sulfide blebs. Note the very small oxygen peak.

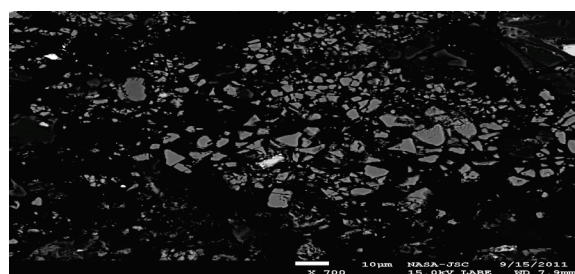


Fig. 3. BSE image of the area in the recovered sample showing angular iron sulfate crystals mixed with basalt particles.

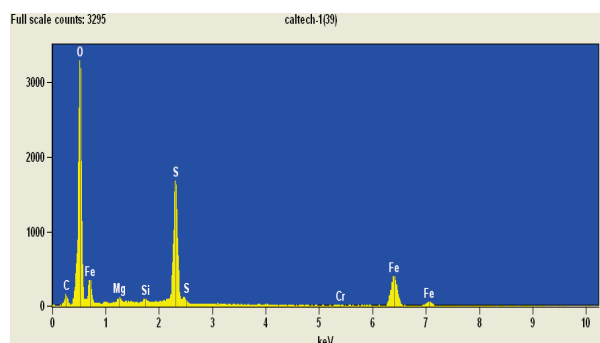


Fig. 4. Typical EDS spectrum of the iron sulfate particles remaining unmelted in the recovered sample. Note the large oxygen peak.